THE FLUORESCENCE, ABSORPTION, AND MAGNETIC ROTATION SPECTRA

OF

POTASSIUM VAPOR.

BY

TAYLOR SCOTT CARTER.

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CONTENTS.

INTRODUCTION.

The recent very exhaustive study of the properties of sodium vapor[1] has shown that our knowledge of the structure of the molecule and of the mechanism of radiation may be increased by the investigation along different lines of metallic vapors. During the investigation the periodicities of the vibrating mechanisms have been studied in a number of ways: by absorption, by exciting the vapor with white or monochromatic light, by cathode ray stimulation, and from the standpoint of the magneto-optical properties of the vapor. The fluorescence spectrum which is shown when the vapor is stimulated by white light is very complex. This spectrum which is channelled and which resembles many emission spectra has a large number of lines.

The very important fact has been brought out that it is possible to analyse this complex spectrum into a number of simple spectra, each one of which may be brought out by exciting the vapor with a monochromatic source of radiation of the proper frequency. The vapor can be excited to fluorescence by monochromatic sources obtained by utilizing certain lines from the arcs of various metals

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1. R. W. Wood: Phil. Mag. Nov. 190[illegible].

such as zinc, cadmium, thallium, lead, silver, bismuth and copper. In each case a series of lines is obtained and in many cases the lines of the series are equally spaced along the spectrum. The superposition of all of these simple spectra gives the white-light fluorescent spectra.

It was further found that any given series of lines could be brought out by exciting the fluorescence with a source of radiation of wave-length corresponding to that of any line in the series, but that certain lines would be absent depending upon the wave-length of the line in the series which was selected.

Sodium vapor in a strong magnetic field has the property of rotating the plane of polarization of light for wave-lengths corresponding to those of certain lines in its absorption spectra, i.e. polarized light which has been passed through magnetized sodium vapor in a sufficiently dense condition and a Nicol's prism set originally for the complete extinction of light gives a bright line spectrum consisting of a large number of sharp lines. Each bright line corresponds to a dark line in the absorption spectrum, but it was found only a very small percentage of the absorption lines

show its rotary power. There are only about sixty lines in this spectrum, which has been called the magnetic rotation spectrum, in comparison with about 1500 lines in the same region in the absorption spectrum. The magnetic rotation spectrum coincides in general with the fluorescent spectrum excited by white light, although there are a great many of the lines absent in the former. The magnetic rotation spectrum contains only about half as many lines as the fluorescent spectrum, the lines, however, are much sharper in the magnetic rotation spectrum. The intensities of the lines are very variable, and apparently bear no relation to the intensities of the corresponding absorption lines.

Five distinct series of lines have been identified in the magnetic rotation spectrum, and these correspond to the series in the fluorescent spectrum brought out by monochromatic stimulation.

In view of the similarity between the emission spectra of Sodium and Potassium, and of the fact that Potassium vapor was known to show a strong fluorescence, it was thought very desirable to extend the Potassium vapor studies along the same line.

HISTORICAL.

The red fluorescence which is exhibited by the vapor of metallic Potassium when it is illuminated with a beam of white light was first observed by Wiedemann & Schmidt[1].

The metal was enclosed in an exhausted glass bulb, heated until vaporization occurred, and a strong beam of sun- or arc- light focussed at the center of the bulb. A red cone of fluorescent light appeared, which, when examined with the spectroscope, showed a red band, the position of which as roughly determined was between wave-lengths 595 and 615 μμ.

GENERAL FACTS.

The vapor has been studied from the standpoint of its absorption, fluorescence, and selective magnetic rotation of the plane of polarization, and it has been possible to obtain photographs of these spectra.

One of the most interesting facts brought out by these investigations is the almost exact similarity between the spectra of Potassium

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1. Wied. Ann. 57, 447, 1896.

vapor and the corresponding spectra which have been shown in the case of Sodium vapor.

During the early part of the experiments the vapor was investigated in glass bulbs of from 5 to 10 centimeters diameter. A very small piece of metal was rolled up and introduced into the bulb, which was then exhausted to a vacuum of about 1 millimeter, and sealed off. During a preliminary study of the conditions under which the fluorescence was exhibited to the best advantage it was found that the glass bulb became blackened after being heated for a very short time. Bulbs of hard glass blown in an oxy-hydrogen flame were then tried and found very satisfactory. They would stand being heated for several hours without becoming much blackened.

FLUORESCENT SPECTRUM.

Method and Apparatus:

The fluorescent light of the vapor was first examined with a two-prism Steinheil spectroscope. The spectrum showed a broad [illegible] band with apparently no structure far out in the red. In order to obtain greater dispersion the light was next examined by means of a large three-prism spectrograph. With this apparatus the spectrum showed considerable structure. Examined visually about fifteen bands

could be distinguished. The fluorescence was bright enough for good negatives of its spectrum to be obtained on the new Wratten & Wainwright Panchromatic plates with exposure of from two to three hours.

The best photograph taken with a width of slit such that the D lines were just resolved on the plate showed that the spectrum was fluted, the flutings, however, not being resolved into lines. The bands were quite sharp on the sides toward the shorter wave-lengths and on the other sides terminated in wings which extended as a fainter dark band up to the next band.

The absorption spectrum photographed with the same apparatus was found to be the compliment of the fluorescent spectrum. When the two negatives were superimposed it was seen that each dark band of the latter was represented by a light band in the former. As it was desirable to work with a much denser vapor than it was possible to obtain with the glass bulbs, the behavior of the metal when heated in a highly exhausted steel tube was studied.

A plain steel tube of 3" diameter and 3' in length was used in the preliminary study. A small piece of brass tubing through which the tube could be exhausted was brazed into one end. Several lumps of

the metal were introduced into the tube and the end closed with glass cemented on with sealing wax. Arc light sent in in a slightly oblique direction was brought to a focus by means of a lens directly over the metal. On heating the tube the red spot of fluorescent light was observed through the opposite end.

The fluorescence was much more intense than had ever been observed with the vapor in the glass bulb.

The arrangement of the apparatus during the subsequent experiments on the fluorescence was exactly the same as that made use of in the work on sodium vapor. The apparatus consisted of a tube of thin steel 3" in diameter and 30" in length with a steel retort which was constructed by fitting two circular disks of steel to a short piece of tubing, at its center, in which about half an ounce of Potassium was placed. The ends of the retort were provided with oval apertures. After the metal was cut up into strips and introduced into the retort the latter was pushed to the center of the tube and the glass plates cemented on. A Fleuss pump was applied to exhaust the tube, which was then heated at the center with a Bunsen flame. The illuminating beam of arc light was brought to a focus just inside of one of the apertures of the retort. By sending the

exciting light in an oblique direction through one end the fluorescence could be observed through the same end against a dark background. With the metal in the retort which prevented its rapid distillation to the colder parts of the tube, it was possible to make exposures of practically any length. The ends of the tube were kept cool by jackets of absorbent cotton, which dipped into pails of water.

By employing higher dispersion an attempt was made to break up the bands which had been photographed with the three-prism spectrograph. The prisms were removed from that apparatus and a plane grating substituted. It was found that this new apparatus gave a first order spectrum about five times as long as the spectrum given by the prism. The lenses used were of 36" focal length. The adjustment was so made that the center of the spectrum fell at the axis of collimation and very good definition was obtained throughout.

With this arrangement of things several very good photographs of the spectrum were obtained. The time of exposure varied from two to three hours. It was possible to measure up on the dividing engine the wave-lengths of about fifty lines by comparing them with standard lines in the iron spectrum. They extend from wave-length [illegible] to [illegible]. It was found that the centers of these bands could be determined

with an accuracy of within half an Angstrom unit. In the region of shorter wave-lengths the bands are all of about the same intensity, and are nearly equally spaced along the spectrum. Between [illegible]415 and [illegible]70 there are eight very strong lines which are about equally distant. They are represented in the magnetic rotation spectrum and are due to the strongest lines in the absorption spectrum. This series will be discussed further under the magnetic rotation spectrum. As we go out into the region of longer wave-lengths the spectrum consists of groups of lines of nearly the same intensity, the lines between the groups becoming fainter and fainter. The lines of this spectrum coincide line by line with the principal lines in the absorption spectrum, although as will be seen, there are a great many more absorption lines. The wave-lengths of the fluorescence measured are given below.

Wave-Lengths.		Wave-Lengths.	
λ		λ	
[illegible].1[illegible]		[illegible]08.0[illegible]	
[illegible]		[illegible]14.[illegible]	
[illegible]		[illegible]21.57	
[illegible]		[illegible].9	
[illegible]3.97		[illegible]3[illegible].0[illegible]	
[illegible]3[illegible].7[illegible]		[illegible]44.3[illegible]	very strong
[illegible]00.[illegible]		[illegible]	
[illegible]07.3		[illegible]0.04	
[illegible]	strong	[illegible]	
[illegible]3.7[illegible]		[illegible]	
[illegible]430.[illegible]		[illegible].19	very strong
[illegible]		[illegible]0.[illegible]	
[illegible]	strong	[illegible].0[illegible]	
[illegible]		[illegible]	
[illegible]1.0[illegible]		[illegible]	
[illegible]		[illegible]1[illegible].[illegible]	
[illegible]74.[illegible]		[illegible]	quite strong
[illegible]		[illegible]	quite strong
[illegible]0.[illegible]		[illegible]	
[illegible].13		[illegible]	
[illegible]		[illegible]	

Wave-Lengths.

λ

[illegible].05

[illegible]3 quite strong

[illegible]70.14 quite strong also

[illegible] quite strong

[illegible]

[illegible]

[illegible]70[illegible].05 quite strong

[illegible]1[illegible]1 " "

[illegible].01 " "

[illegible].17 " "

[illegible]1.[illegible] " "

[illegible] " "

We have seen that, considered roughly, the fluorescent spectrum covers the region of absorption. An attempt was made to study the relation between the wave-length of the absorbed and emitted light by means of a Heuss monochromatic illuminator. This apparatus enables one to cut out a region of any width from a continuous spectrum, and to focus this light on the vapor.

The method was to find by changing the wave-length of the exciting light the region of absorption which gave the maximum intensity of fluorescence, and by narrowing the slit of the illuminator as far as was consistent with the fluorescence to isolate, if possible, an approximately monochromatic source of excitation. The wave-length of the exciting light was increased by turning the graduated screw which rotated the prisms of the instrument, and it was found that there was a wide region which would excite the fluorescence. The spectrum examined with the Steinheil spectroscope was, however, so feeble as to be hardly observable and little was learned from this method of study.

The zinc arc was then tried for a monochromatic source. The light from the arc formed in air between a carbon electrode and a small crucible [illegible] pieces of zinc were fed, was [illegible]

focus just within the aperture of the retort containing the metal. This arc gave a very intense and strongly concentrated source of light from which the single line 6363 was utilized. It was found that a strong fluorescence was excited by this line. Examined visually with a grating spectroscope a series of lines apparently equally spaced in the spectrum were observed.

The great difficulty in working with the arc in air is that the position of the crater changes constantly, making it almost impossible to keep the spot of fluorescent light on the slit of the spectrograph for any length of time. The spectrum of the fluorescent light brought out by exciting with the zinc arc has not been photographed.

ABSORPTION SPECTRUM.

The photographs of absorption spectra taken with the vapor in the cell never showed very strong absorption for the reason that it was impossible to get the vapor sufficiently dense. With the steel tube it was possible to work with a very dense vapor, and with the greater dispersion given by the grating spectrograph, excellent photographs have been taken of the absorption spectra.

A lump of potassium was placed at the center of the tube, and

ends were cemented on and the tube exhausted as in the previous experiments. The tube was supported in a horizontal position in front of the slit of the spectrograph, and light from the arc sent through the tube was brought to a focus on the slit. By regulating the flow of gas to the burner, placed below and at the center of the tube, it was possible to observe the spectrum for any degree of density of the vapor. Photographs were taken at different densities.

The heads of the bands appear first, and as the density increases the fire lines of which they are formed develop in succession. With a sufficiently dense vapor the spectrum consists of a very large number of fine black lines. The wave-lengths of the strong bands and principal lines of the absorption spectrum are given below.

Wave-Lengths.	Wave-lengths.
λ	λ
[illegible].[illegible]3	[illegible] very strong
[illegible]	[illegible] strong
[illegible] strong	[illegible]05.[illegible] strong
[illegible]21.74	[illegible]1[illegible] "
[illegible]2[illegible] strong	[illegible]0.[illegible] "
[illegible]34.3[illegible] "	[illegible]34.36
[illegible] "	[illegible]4.[illegible] very strong
[illegible].0[illegible] "	[illegible]
[illegible].[illegible]1 very strong	[illegible]
[illegible]0.1[illegible]	[illegible]
[illegible] very strong	[illegible]3.9[illegible] very strong
[illegible]	[illegible].[illegible]
[illegible]	[illegible]0[illegible]
[illegible]1[illegible] strong	[illegible]1[illegible]
[illegible]0.[illegible] strong	[illegible] strong
[illegible]	[illegible]
[illegible].27 very strong	[illegible]3

Wave-Lengths.

λ	
[illegible].[illegible]	strong
[illegible].52	"
[illegible].1	
[illegible].[illegible]	
[illegible]	
[illegible]71[illegible].[illegible]	strong
[illegible]1.[illegible]2	
[illegible].3[illegible]	
[illegible]	
[illegible].[illegible]	
[illegible]4.[illegible]	
[illegible]1.3[illegible]	
[illegible].[illegible]	
[illegible].[illegible]	

MAGNETIC ROTATION SPECTRUM.

Method and Apparatus:

The magnetic rotation properties of potassium vapor were first investigated in the following way: A glass bulb [illegible] and then filled, exhausted and sealed off was suspended between the conical pole pieces of a large electromagnet. Light from an arc lamp rendered parallel by a lens was passed in succession through a Nicol prism, the hollow cores of the magnet, the bulb containing the metal, and a second Nicol, after which it was brought to a focus by a second lens on the slit of the grating spectroscope. The Nicols were set for complete extinction of the light so that the field was dark. The bulb was heated by a Bunsen flame until the metal was vaporized, and the field of the magnet produced. On looking into the spectrograph a faint yellow light was observed and the rotation in the vicinity of the D lines due to the presence of sodium. No rotation lines in the red were observed. On repeating the experiment, however, with the vapor in a steel tube, a bright line rotation spectrum was discovered.

A piece of steel tubing of such diameter as to slip into the hollow cores of the magnet from which the pole pieces had been re-

[illegible] was used. The tube was exhausted through a short brass tube sealed into one of its ends. The tube was introduced into the [illegible] and one of its ends closed with a piece of plate glass cemented to it with sealing wax. Through the open end was introduced a lump of potassium and pushed to the center of the tube. The open end was then closed in a similar manner. The tube was connected with the mechanical pump which gave a vacuum of a millimeter or two. Parallel light was sent through the tube, nicols, etc. as described above, and focussed on the slit. With the current off the height of a flame placed beneath the center of the tube was regulated so that the absorption lines were brought out strong and black. The nicol was then set for complete extinction. On exciting the magnet there appeared in addition to the bright rotation lines D & D_2 a number of bright lines in the red. It was found that the rotation spectrum was very sensitive to changes in the density of the vapor. The least variation in the height of the flame would destroy the spectrum. Electrical heating of a porcelain tube containing the metal was tried, but it was found that the density could be kept more constant by working with a steel tube and heating with a Bunsen [illegible]

Several photographs of the rotation spectrum were taken. About twenty-five lines could be measured on the best plate. One was taken with the absorption spectrum on the same plate and shows the eight strong lines [illegible] mentioned in connection with the fluorescent spectrum. The plate shows that they coincide with the strong heads of the absorption bands. Six of these strong lines could easily be picked out as a series of lines, very nearly equidistant along the spectrum. Their wave-lengths are:

λ		λ differences.
[illegible].05		
		[illegible].69
5412.71		
		20.[illegible]
[illegible].[illegible]		
		20.[illegible]1
[illegible].21		
		20.[illegible]
[illegible]50[illegible].0[illegible]		
	$\frac{[illegible]0.[illegible]}{2}$	[illegible]0.[illegible]
[illegible]		

There are three strong lines which do not fall in this series:

[illegible]512.[illegible] [illegible]543.[illegible] [illegible].[illegible]

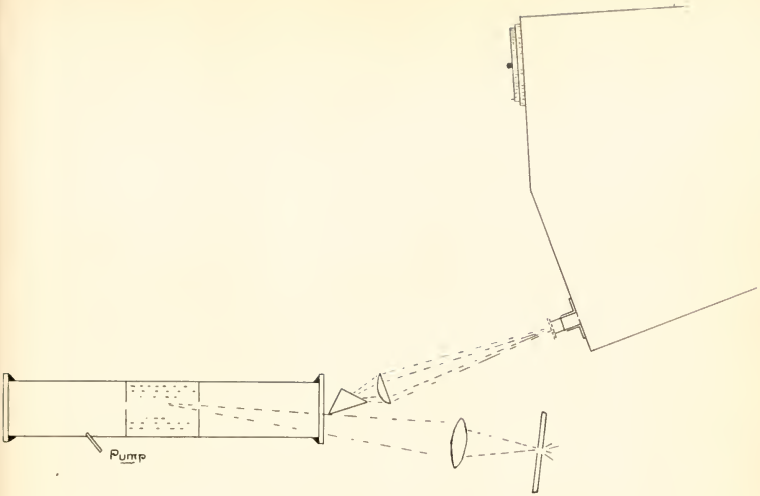
The other lines are all of about the same intensity. [illegible]

absorption lines, a fact which was found to hold in the magnetic rotation spectrum of sodium vapor. Some of the strongest lines in this region show no rotation. The wave-lengths of the lines that could be measured here are:

λ		λ	
62[illegible].03		[illegible].21	strong
[illegible]		[illegible].89	
[illegible]315.5[illegible]		[illegible]05.00	strong
[illegible]5.		[illegible]1[illegible].[illegible]	"
[illegible].13		6[illegible]43.[illegible]	"
[illegible].41		[illegible]	
[illegible]1.		[illegible].01	strong
[illegible]54.[illegible]		[illegible]	"
[illegible].02	strong	[illegible]01.7	
[illegible]1.15		[illegible]	
[illegible].71	strong	[illegible].35	
[illegible]20.43			
[illegible]	strong		

BIOGRAPHICAL NOTE.

Taylor Scott Carter was born near Marshall, Virginia on the [illegible] of July 1[illegible]. He received his early education under a private tutor at his home, and in the fall of 189[illegible] he entered Bethel Military Academy near Warrenton, Va. There he remained one year, and then matriculated at the Virginia Military Institute, from which institution he was graduated in June 1901 with the degree of Bachelor of Science. The next year he was instructor in Physics and Mathematics at the New Mexico Military Institute, Roswell, N. M. In the fall of 190[illegible] he was appointed Assistant Professor of Mathematics and Mechanical Drawing at the Virginia Military Institute. He entered the graduate department of Physics at the Johns Hopkins University in the fall of 1904, taking Physical Chemistry and Mathematics as first and second subordinates respectively. During his course at the University he pursued his studies in Physics under Professors Ames, Wood and Bliss; in Applied Electricity under Dr. Whitehead; in Physical Chemistry under Professor Jones, and in Mathematics under Dr. Cohen. He held a Hopkins Scholarship from Virginia during his three years residence at the University.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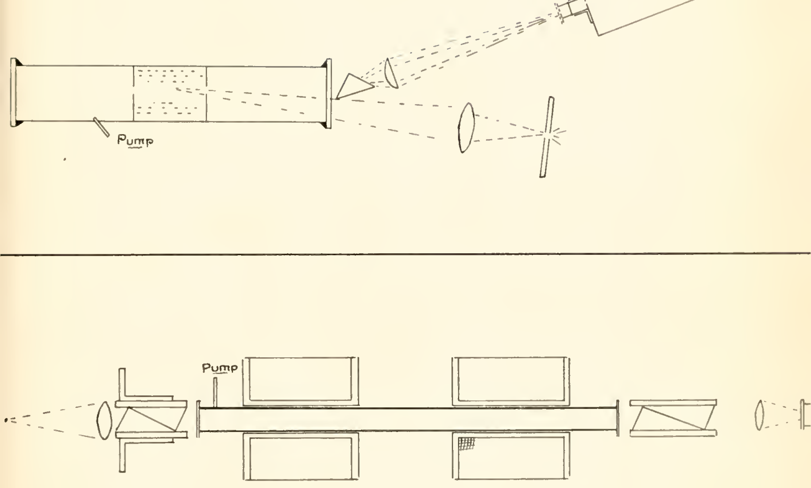
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